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Thermal variation of different specific heat components of potassium europium fluoride

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Abstract . The present paper reports the thermal variation of different specific heat components of potassium europium fluoride (PEF) which is a paramagnetic insulator at room temperature. Its lattice specific heat was calculated by adopting the empirical formula applicable for $Eu(OH)_3$. Using the crystal field energy levels of the sample, its Schottky specific heat has been calculated between 10K and 300K. The nuclear hyperfine levels for ^{151}Eu nucleus in PEF have been determined for nuclear ground (I_g = 5/2) as well as for first excited state (I_e = 7/2). The hyperfine specific heat shows an inverse T^2 rule, where T represents temperature between 10 mK and 1K.

Keywords Crystal field, Schottky specific heat, hyperfine interaction.

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1. Introduction

The complete fluorescence spectra of diluted potassium europium fluoride (PEF : Eu^{3+} in KY_3F_{10} matrix) in visible and IR range have been reported earlier [1]. By adopting the crystal field (CF) theory, the energy levels of low-lying terms of Eu^{3+} (*i.e.*, $^7F_1$, $^7F_2$ and $^7F_3$) in the above system have been explained in our recent paper [2], and the CF parameters have been determined accurately. From the calculated CF energy levels and CF wavefunctions we have estimated the thermal variation of magnetic susceptibility and their anisotropy over a wide range of temperature below room temperature (RT).

Unlike magnetic property, the thermal property of this type of insulator is isotropic in nature. But the Schottky specific heat (C_{sh}) of these compounds depends totally on the CF energy level pattern. The present paper reports the thermal variation of different specific heat components of PEF. These components have been calculated considering that the system would crystallize in structure similar to that of KY_3F_{10}. To explore whether any interesting thermal property exists or not in the system, specially at low temperature region, the nuclear hyperfine specific heat (C_{hf}) has been studied theoretically.

2. Theoretical considerations

The total specific heat of a rare-earth (RE) paramagnetic insulator consists of several components as

$$C_T = C_L + C_{sh} + C_M + C_{hf}, \qquad (1)$$

where C_L is the lattice specific heat, C_{sh} represents Schottky specific heat, C_M is magnetic specific heat and C_{hf} arises due to hyperfine interaction on the nucleus of RE ion in solid.

Chirico and Westrum [3] derived a relation of C_L for RE-hydroxides where C_L for all RE-hydroxides can be calculated by using the measured total specific heat value of $La(OH)_3$ and $Gd(OH)_3$. Applying the same relation and using the measured specific heats of $La(OH)_3$ and $Gd(OH)_3$, we can approximately estimate the lattice specific heat of this compound above RT.

Between RT and 10K, where the CF effects play the most important role in the solid, C_{sh} becomes interesting. The thermal variation of C_{sh} for this compound has been calculated with the CF energy pattern using the standard formula [4] :

$$C_{sh} = \frac{R}{Z^2}\left[Z\sum_{i=1}^{n}(x_i)^2\exp(-x_i) - \left\{\sum_{i=1}^{n}x_i\exp(-x_i)\right\}\right], \qquad (2)$$

where R has the value close to the universal gas constant, and $x_i = E_i^{(0)} / KT$, Z the partition function $\sum \exp(-x_i)$ and $E_i^{(0)}$ are the CF eigenvalues of $^7F_1$, $^7F_2$, $^7F_3$ in the sample.

Below 10K, the other component of specific heat *i.e.*, magnetic specific heat (C_M) becomes important. For non-magnetic ground state $^7F_0$, the contribution of magnetic specific heat of the sample is nil and no magnetic ordering has been found in this type of Eu^{3+} compounds [5].

Around 1K and in millikelvin region, the specific heat of this type of RE solids arises due to hyperfine (HF) interaction in the nucleus of RE^{3+} ion. The corresponding specific heat is hyperfine specific heat (C_{hf}). It has been observed [4,5] that the magnitude of C_{hf} is appreciable in case of RE^{3+} ions in insulators since most of the nuclei of RE ions have large values of isotopic spins and low-lying nuclear excited states. The hyperfine Hamiltonian H_{hf} is given by

$$H_{hf} = AI_zS_z + B(I_xS_x + I_yS_y) + P\left[3I_z^2 - I(I+1)\right], \quad (3)$$

where A and B are HF constants, P is called the quadrupolar interaction parameter, I and S represent nuclear and electronic spins respectively. For Eu^{3+} ion in PEF the electronic ground term is a nonmagnetic $^7F_0$ hence nuclear magnetic interaction is zero. P has mainly two parts, P_l (lattice) and P_{4f} (4*f*-electronic part) arising from four significant sources [5]. Hence,

$$P = P_l + P_{4f} \text{ and}$$

$$P_l = -\frac{3Q}{I(I+1)} \frac{(I-\gamma_\infty)}{(I-\sigma_2)} \left\langle \gamma^{-3} \right\rangle_{4f} - B_2^0 \text{ and}$$

$$P_{4f} = \frac{6e^2Q(1-\sigma_2)}{I(2I-1)\Delta_2} \left\langle \gamma^{-3} \right\rangle_{4f} \left| \left\langle 20 \| \alpha \| 00 \right\rangle \right|^2,$$

where Q is the quadrupole moment of the nucleus, γ_∞ and σ_2 are the lattice antishielding and atomic shielding factors respectively. Δ_2 is the energy difference between $J = 0$ and $J = 2$ states of Eu^{3+} in PEF.

Operating by H_{hf} on basis states $|I, m_I\rangle$, HF energy levels for ground as well as for first excited state for ^{151}Eu can be determined. The HF specific heat was calculated using eq. (2) where E_i represent now the eigenvalues of the HF-split levels of nuclear ground state.

3. Results and discussion

PEF is a tetragonal compound. In solid structure, each Eu^{3+} ion is surrounded by eight F^- ions. Two square planes each containing four F^- ions are rotated relative to each other by 45°. The line joining the two planes containing the Eu^{3+} and perpendicular to the two planes is almost parallel to *c* axis (Figure 1).

In empirical formula derived by Chirico and Westrum (Jr) [3], there is a factor represented by *f*. It was observed that the value of *f* increased linearly with the number of 4f-electrons in

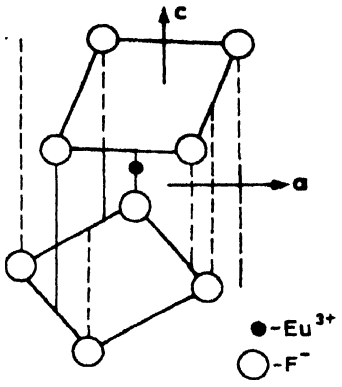

Figure 1. First order neighbour of Eu^{3+} in PEF

lanthanides [4]. Considering that the structure of PEF would be similar to that of KY_3F_{10}, the *f*-factor for potassium europium fluoride was determined, and we calculated the thermal variation of C_L for PEF from 10K to 300K (Figure 2).

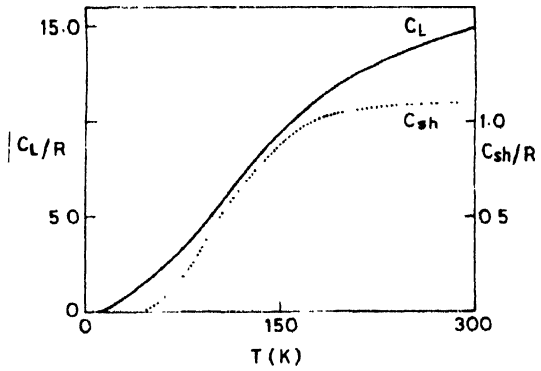

Figure 2. Thermal variation of C_L and C_{sh}.

Using the CF energy pattern [2] we have calculated the thermal variation of C_{sh} between 5K and 300K (Figure 2). At 300K the value of C_{sh} is only 6.67% of that of C_L.

It was mentioned earlier that Eu^{3+} has a nonmagnetic ground term $^7F_0$. The position of first CF energy level is at about 261 cm^{-1} which corresponds to 375K. Hence below RT down to 1K, the electronic population is mainly in ground term and for this reason, the magnetic component of specific heat for the sample is nil.

The nuclear spin for $^{151}Eu^{3+}$ ion in ground state is 5/2. It is followed by the first excited state ($I_e = 7/2$) which is situated at about 21.6 Kev above I_g. In our recent paper, we have shown that due to quadrupole interaction of the nuclear spins of $^{151}Eu^{3+}$ embedded in PEF crystal, the ground state I_g is split into three doublets. These states have relative energies as 0, $28.856 \times 10^{-4} cm^{-1}$ and $43.284 \times 10^{-4} cm^{-1}$. The corresponding eigenstates (designed by m_I values) are $|\pm 5/2\rangle$, $|\pm 3/2\rangle$ and $|\pm 1/2\rangle$ respectively.

The HF specific heat was computed with the help of eq. (2) using HF-split level pattern of the ground state ($I_g = 5/2$). The thermal variation of C_{hf} in millikelvin region (Figure 3) shows that C_{hf}/R has a maximum value of 0.767 at about 2mK. C_{hf}/R follows an inverse T^2 rule (where T represents temperature in absolute scale) *i.e.*, $C_{hf}/R = 12.42 \times 10^{-6}T^2$ between 10 mK and 1K.

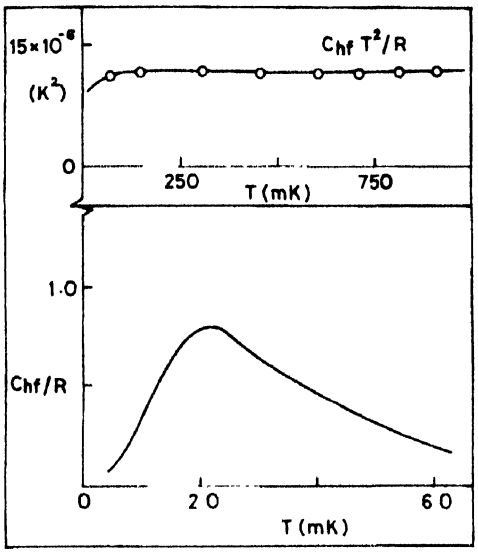

Figure 3. Thermal variation of C_{hf} in mK range

The relation $C_{hf}/R = 12.42 \times 10^{-6}T^2$ bears an important property. It has been previously observed that magnetically diluted crystals of cerium diglycollate was proposed as an efficient magnetic material for millikelvin thermometry and refrigeration [6]. Since Eu^{3+} has a nonmagnetic ground state $^7F_0$, the conventional magnetic ordering is absent in this type of sample. Again if it follows the same structure of KY_3F_{10} then $Eu^{3+} - Eu^{3+}$ distance would be comparatively large in PEF, forbidding magnetic ordering. Hence the above property shown by ^{151}Eu enriched PEF, may be utilized in millikelvin thermometry. Measurements of specific heat of PEF crystal at different temperatures are welcome.

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